

Synthesis, Structure and Characterization of a 3D Chiral Indium Carboxylate Metal-organic Framework Based on 1,1'-Biphenol Ligand

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ABSTRACT A novel indium-based chiral metal organic-framework **1** $\{\text{In}_2\text{L}(\mu_2\text{-O})(\text{H}_2\text{O})_3\}_n$ was synthesized from C_2 -symmetric 1,1'-biphenol-based ligand H_4L and structurally characterized by single-crystal and powder X-ray diffraction, Fourier-transform infrared spectra (FTIR), solid-state circular dichroism (CD) and thermal gravimetric analysis (TGA). **1** crystallizes in monoclinic space group $P2_1$ with $a = 10.1861(5)$, $b = 18.5632(9)$, $c = 16.5153(8)$ Å, $V = 3077.1(3)$ Å³, $Z = 2$, $M_r = 944.29$ g/mol, $D_c = 1.019$ g/cm³, $F(000) = 944$, $GOOF = 0.932$, the final $R = 0.0577$ and $wR = 0.1091$ for 22090 observed reflections with $I > 2\sigma(I)$. Each In_2 cluster in **1** is linked by four ligands and each ligand is coordinated to four In_2 clusters to generate a 3D network. Additionally, the photoluminescence of **1** and H_4L were also investigated.

Keywords: 1,1'-biphenol, indium; chiral metal-organic framework; photoluminescence;

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1 INTRODUCTION

Metal-organic frameworks (MOFs) and porous coordination polymers (CPs) have received great attention not only because of their various structural topologies and chemical tunabilities but also of their several useful properties and applications, such as gas storage, gas separation, catalysis, drug delivery, sensing, and recognition^[1-13].

A large effort has been devoted to the study on the reactivity of the first row of divalent transition metals

(e.g., Cu^{2+} , Zn^{2+}), but less work has reported the synthesis of MOF-type compounds incorporating trivalent metals, especially for the *p* elements of the periodic table such as aluminum, gallium, or indium^[14-22]. As heterogeneous Lewis acid catalysts, they have the advantages of low toxicity and high selectivity which can make a variety of organic reactions carry out smoothly under mild conditions. This is in line with the requirements of green chemistry and shows a good prospect. On the other hand, 1,1'-biphenol derivatives with intrinsic C_2 symmetry have long been known as one of the privileged chiral ligands^[23-27]. Herein we report the synthesis, structure, thermal stability and photoluminescence of 1,1'-biphenol-based indium framework.

2 EXPERIMENTAL

2.1 Materials and apparatus

All of the chemicals are commercially available, and used without further purification. The IR (KBr pellet) spectra were recorded (400~4000 cm^{-1} region) on a Nicolet Magna 750 FT-IR spectrometer. TGA were carried out in N_2 atmosphere at a heating rate of 10 $^\circ\text{C min}^{-1}$ on a STA449C integration thermal analyzer. The fluorescence spectra were carried out on a LS 50B Luminescence Spectrometer (Perkin Elmer, Inc., USA). The CD spectra were recorded on a J-800 spectropolarimeter (Jasco, Japan)

2.2 Synthesis of **1**

A mixture of InCl_3 (13.2 mg, 0.06 mmol), H_4L (19.6 mg, 0.03 mmol), DMF (0.5 mL), DMSO (1.4 mL), THF (5.6 mL), H_2O (2.8 mL) and HOAc (0.2 mL) in a capped vial was heated at 100 $^\circ\text{C}$ for 24 h. Colourless crystals of **1** were filtered, washed with THF and Et_2O respectively, and dried at room temperature. Yield: 23.6 mg (72%). FTIR (KBr pellet, ν/cm^{-1}): 509 (w), 586 (w), 640 (w), 663 (w), 679 (w), 711 (m), 719 (m), 732 (m), 760 (m), 780 (s), 838 (w), 880 (w), 896 (w), 951 (m), 994 (w), 1025 (s), 1091 (w), 1127 (w), 1171 (m), 1213 (w), 1254 (w), 1305 (w), 1366 (s), 1435 (s), 1458 (s), 1467 (s), 1497 (w), 1507 (w), 1582 (s), 1627 (s), 1654 (w), 1663 (w), 1692 (w), 1697 (w), 1753 (w), 1769 (w), 1867 (w), 2189 (w), 2461 (w), 2786 (w), 2869 (s), 2921 (s), 2961 (s), 2992 (w), 3406 (s), 3508 (s), 3741 (w), 3883 (w).

2.3 Crystallographic measurements and structure determination

Single-crystal XRD data for **1** were collected on a Bruker APEX-II CCD diffractometer with graphite-monochromatic $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 173.15 K. The structure was solved by direct

methods with SHELXS-2014 and refined with SHELXL-2014^[28] using *OLEX 2.0*^[29]. All the non-hydrogen atoms except guest molecules were refined by full-matrix least-squares techniques with anisotropic displacement parameters and the hydrogen atoms were geometrically fixed at the calculated positions attached to their parent atoms, and treated as riding atoms, whereas the guest water was refined isotropically and no hydrogen atoms were added. For **1**, the final $R = 0.0577$, and $wR = 0.1091$ ($w = 1/[\sigma^2(F_o^2) + (0.1117P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$), $S = 0.932$, $(\Delta/\sigma)_{\max} = 0.001$, $(\Delta\rho)_{\max} = 0.981$ and $(\Delta\rho)_{\min} = -0.520$ e/Å³. The selected bond lengths and bond angles are given in Table 1.

2.4 Structure determination

Table 1. Selected Bond Lengths (Å) and Bond Angles (°)

Bond	Dist.	Bond	Dist.	Bond	Dist.
In(1)–O(2)#1	2.094(9)	In(1)–O(1W)	2.147(11)	In(1)–O(5)	2.061(8)
In(1)–O(7)#2	2.168(9)	In(1)–O(2W)	2.170(11)	In(1)–O(8)	2.087(10)
In(2)–O(1)	2.183(9)	In(2)–O(3W)	2.396(6)	In(2)–O(3)#3	2.228(6)
In(2)–O(4)#3	2.213(7)	In(2)–O(5)	2.101(8)	In(2)–O(6)#2	2.134(8)
Angle	(°)	Angle	(°)	Angle	(°)
O(2)#1–In(1)–O(1W)	83.0(3)	O(2)#1–In(1)–O(7)#2	88.9(4)	O(2)#1–In(1)–O(2W)	91.9(4)
O(1W)–In(1)–O(7)#2	89.7(5)	O(1W)–In(1)–O(2W)	90.2(5)	O(5)–In(1)–O(2)#1	102.3(4)
O(5)–In(1)–O(1W)	174.7(4)	O(5)–In(1)–O(7)#2	90.1(4)	O(5)–In(1)–O(2W)	89.9(4)
O(5)–In(1)–O(8)	89.8(4)	O(7)#2–In(1)–O(2W)	179.2(5)	O(8)–In(1)–O(2)#1	167.9(4)
O(8)–In(1)–O(1W)	84.9(4)	O(8)–In(1)–O(7)#2	90.0(4)	O(8)–In(1)–O(2W)	89.2(5)
O(1)–In(2)–O(3W)	175.5(3)	O(1)–In(2)–O(3)#3	82.4(4)	O(1)–In(2)–O(4)#3	82.1(3)
O(3)#3–In(2)–O(3W)	95.4(3)	O(4)#3–In(2)–O(3W)	93.4(3)	O(4)#3–In(2)–O(3)#3	58.0(3)
O(5)–In(2)–O(1)	89.8(4)	O(5)–In(2)–O(3W)	94.5(3)	O(5)–In(2)–O(3)#3	102.7(3)
O(5)–In(2)–O(4)#3	159.9(3)	O(5)–In(2)–O(6)#2	102.4(3)	O(6)#2–In(2)–O(1)	86.9(4)
O(6)#2–In(2)–O(3W)	93.3(3)	O(6)#2–In(2)–O(3)#3	152.6(3)	O(6)#2–In(2)–O(4)#3	95.6(3)

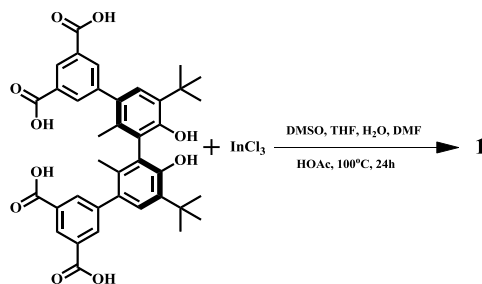
Symmetry transformation: #1: $-x-3, y+1/2, -z+2$; #2: $-x-3, y+1/2, -z+1$; #3: $-x-2, y+1/2, -z+1$; #4: $-x-3, y-1/2, -z+2$; #5: $-x-2, y-1/2, -z+1$; #6: $-x-3, y-1/2, -z+1$

3 RESULTS AND DISCUSSION

3.1 Synthesis and characterization of **1**

As shown in Scheme 1, MOF **1** was synthesized through hydro/solvothermal reactions between InCl₃ and tetracarboxyl-functionalized 1,1'-biphenol ligand H₄L. The absorption peak at 3406 cm⁻¹ in IR spectrum for **1**

could be assigned to $\nu_{\text{as}}(-\text{OH})$ stretching vibration, while the characteristic peaks for C–O stretching vibration could be easily found in the relatively lower band (1171 cm^{-1}). The phase purity was established by the general agreement between the experimental and simulated X-ray powder diffraction patterns (Fig. 1). CD spectra of **1** made from *R* and *S* enantiomers of the H₄L ligand are mirror images of each other, indicative of the enantiomeric nature (Fig. 2). The thermogravimetric analysis of **1** was investigated under a N₂ atmosphere from 50 to 800 °C, and the result indicates that **1** can be stable up to 300 °C (Fig. 3).



Scheme 1. Synthesis of **1**

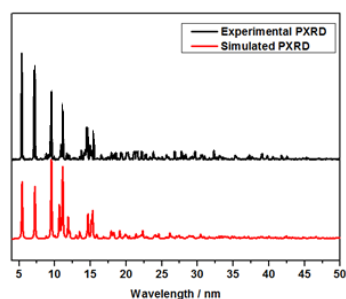


Fig. 1. Simulated and experimental PXRD patterns of **1**

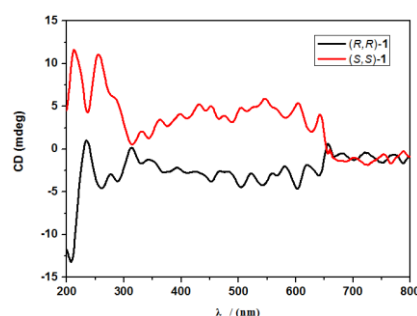


Fig. 2. CD spectra of (*R,R*)/(*S,S*)-**1**

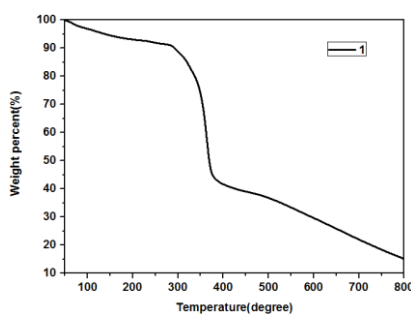
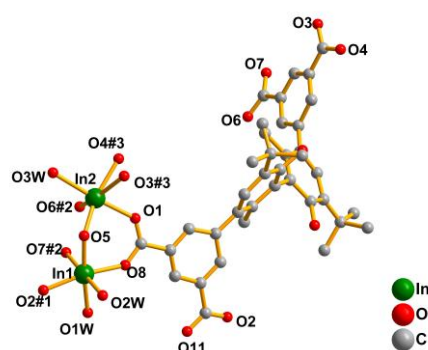


Fig. 3. Thermal analysis curve of **1**

3.2 Structural description

Single-crystal X-ray diffraction study reveals that **1** crystallizes in chiral monoclinic space group $P2_1$. The basic building block is a near-linear dimeric $[\text{In}_2(\text{O}_2\text{C})_4(\mu_2\text{-O})(\text{H}_2\text{O})_3]$ unit, with a C_2 axis passing through one

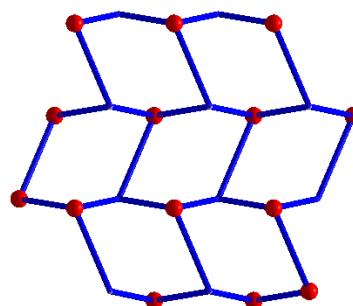
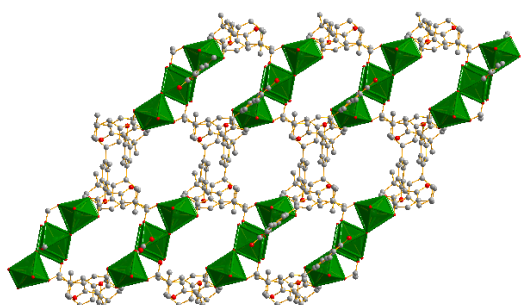
metal center, clustered by one monodentate and three carboxylate groups from four different 1,1'-biphenol units. As illustrated in Fig. 4(a), the asymmetric unit contains two In^{3+} , one **L**, and three coordinated water molecules as well as one $\mu_2\text{-O}$. The In1 is six-coordinated to six oxygen atoms, with three from three different carboxylate groups, one from $\mu_2\text{-O}$ and two from coordinated water molecules, while the In2 coordinates to six oxygen atoms, including four carboxyl oxygen atoms from three different ligands, one oxygen atom from $\mu_2\text{-O}$, and one coordinated water molecule. The In–O bond lengths range from 2.061(8) to 2.396(6) Å, which are quite normal for six-coordinated In ions^[30]. Each dinuclear In_2 cluster in **1** in Fig. 4(b) is thus linked by four 1,1'-biphenol ligands, and each 1,1'-biphenol ligand is linked to four In_2 clusters to generate a chiral 3D network (Fig. 5a). The 3D network can be simplified as the topology for **1** if considering the dimeric In_2 cluster ions as four-coordinating nodes and the H_4L ligands as a tetra-dental linker (Fig. 5b). *PLATON* calculations indicated that **1** contains roughly 50% void space available for guest inclusion.



(a)

(b)

Fig. 4. Coordination mode for In (a) and dimeric In_2 cluster ions as four-coordinating nodes (b). Hydrogen atoms and guest molecules are omitted for clarity. Symmetric codes: #1: $-x-3, y+1/2, -z+2$; #2: $-x-3, y+1/2, -z+1$; #3: $-x-2, y+1/2, -z+1$



(a)

(b)

Fig. 5. 3D framework along the *b* axis (a) and the simplified topology (b) in **1**

3.3 Photoluminescence

Upon excitation at 346 nm, as shown in Fig. 6, the free ligand H₄L displays a fluorescent emission at 435 nm, while the emission of **1** excited at 423 nm exhibits blue-shift of about 12 nm. Due to the d^{10} configuration closed shell electronic configuration, the In atom is difficult to oxidize or reduce. Therefore, the most possible explanation for blue-shift of **1** is the intraligand charge transfer rather than the metal-to-ligand or ligand-to-metal charge transfer^[31].

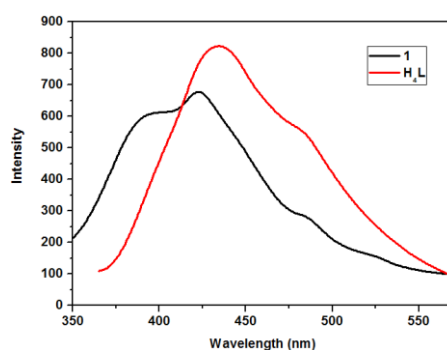


Fig. 6. Fluorescent emission spectra of H₄L and **1**

4 CONCLUSION

In conclusion, we have synthesized a 1,1'-biphenol-based chiral metal-organic framework with indium. It has been characterized by single-crystal, powder X-ray diffraction, CD and TGA. In addition, the photoluminescence of **1** and the free ligand was also studied.

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We report the synthesis, structure, thermal stability and photoluminescence of 1,1'-biphenol-based indium framework, in which each dinuclear In_2 cluster is linked by four 1,1'-biphenol ligands, and each 1,1'-biphenol ligand is linked to four In_2 clusters to generate a chiral 3D network.

